



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :

C23C 16/44

A3

(11) International Publication Number:

WO 99/29917

(43) International Publication Date:

17 June 1999 (17.06.99)

(21) International Application Number: PCT/GB98/03636

(22) International Filing Date: 7 December 1998 (07.12.98)

(30) Priority Data:

9725878.4

5 December 1997 (05.12.97)

GB

(71) Applicant (for all designated States except US): IMPE-
RIAL COLLEGE OF SCIENCE, TECHNOLOGY AND
MEDICINE [GB/GB]; Sherfield Building, Exhibition Road,
London SW7 2AZ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CHOY, Kwang-Leong
[MY/GB]; 35 Blondvil Street, Cheylesmeore, Coventry CB3
5EQ (GB). CHANG, Isaac, Tsz, Hong [GB/GB]; School
of Metallurgy and Materials, University of Birmingham,
Edgbaston, Birmingham B15 2TT (GB).(74) Agent: TURNER, James, Arthur, D. Young & Co., 21 New
Fetter Lane, London EC4A 1DA (GB).(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP,
KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK,
MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU,
ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG,
ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI,
FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE,
SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims
and to be republished in the event of the receipt of amendments.

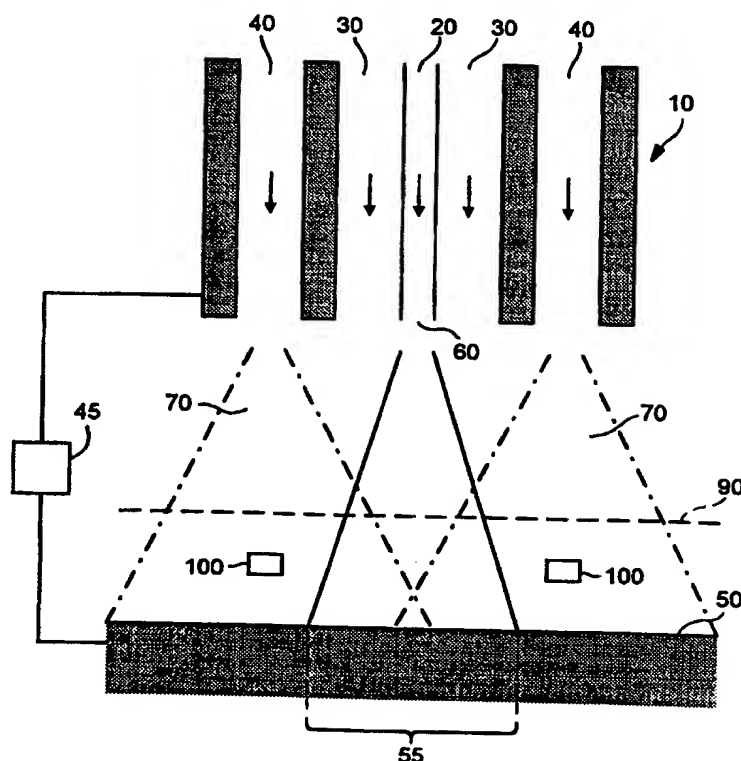
(88) Date of publication of the international search report:

22 July 1999 (22.07.99)

(54) Title: MATERIAL DEPOSITION

(57) Abstract

A method of depositing a material on a substrate comprises the steps of: (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate; (b) applying an electric field between the outlet and the substrate; and (c) generating a flame between the outlet and the substrate (50) so that the stream of droplets of the precursor liquid from the outlet (60) pass through the flame before reaching the substrate (50).



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/GB 98/03636

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C16/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 005, no. 054 (C-050), 15 April 1981 & JP 56 005337 A (HITACHI LTD; OTHERS: 01), 20 January 1981	1,2,6,7, 9-12,16
Y	see abstract	3,4,14, 15
A	---	8
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 143 (C-117), 3 August 1982 & JP 57 067038 A (NIPPON TELEGR & TELEPH CORP), 23 April 1982 see abstract	1,2,6,9, 16
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 May 1999

Date of mailing of the international search report

02/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ekhult, H

INTERNATIONAL SEARCH REPORT

In ternational Application No

PCT/GB 98/03636

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 098, no. 001, 30 January 1998 & JP 09 235131 A (SHOWA ELECTRIC WIRE &CABLE CO LTD; NIPPON TELEG & TELEPH CORP), 9 September 1997 see abstract ----	3,4
Y	PATENT ABSTRACTS OF JAPAN vol. 014, no. 227 (C-0718), 15 May 1990 & JP 02 055241 A (HITACHI CABLE LTD), 23 February 1990 see abstract ----	14,15
A	WO 97 21848 A (BAI WEI ;CHOY KWANG LEONG (GB); IMPERIAL COLLEGE (GB)) 19 June 1997 cited in the application ----	5
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 262 (C-608), 16 June 1989 & JP 01 065040 A (SUMITOMO ELECTRIC IND LTD), 10 March 1989 see abstract -----	13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/03636

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9721848 A	19-06-1997	GB 2308132 A	18-06-1997
		AU 1182997 A	03-07-1997
		CA 2240625 A	19-06-1997
		EP 0870075 A	14-10-1998
<hr/>			



1

2



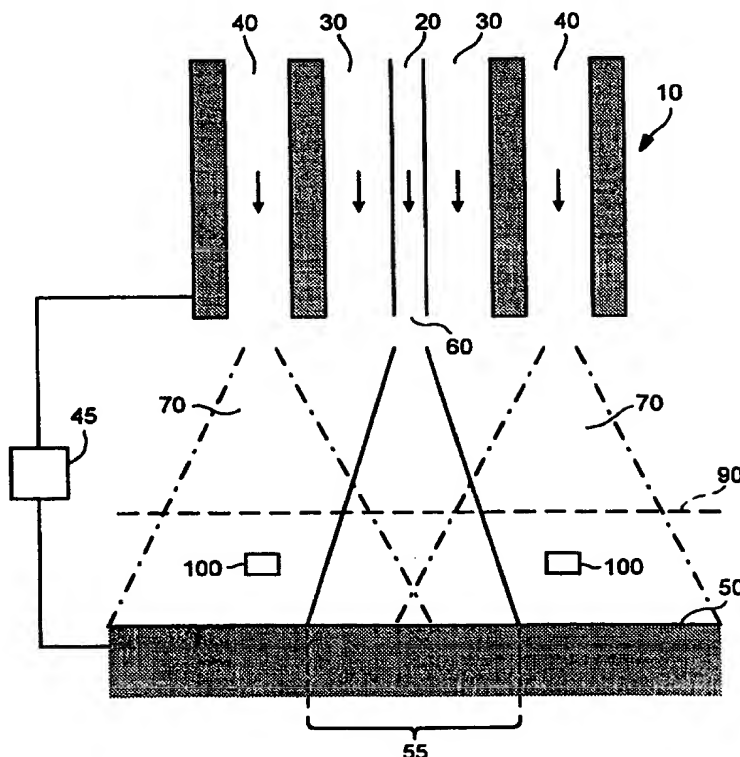
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C		A2	(11) International Publication Number: WO 99/29917
			(43) International Publication Date: 17 June 1999 (17.06.99)
(21) International Application Number: PCT/GB98/03636 (22) International Filing Date: 7 December 1998 (07.12.98) (30) Priority Data: 9725878.4 5 December 1997 (05.12.97) GB (71) Applicant (for all designated States except US): IMPE- RIAL COLLEGE OF SCIENCE, TECHNOLOGY AND MEDICINE [GB/GB]; Sheffield Building, Exhibition Road, London SW7 2AZ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): CHOY, Kwang-Leong [MY/GB]; 35 Blondvil Street, Cheylesmeore, Coventry CB3 5EQ (GB). CHANG, Isaac, Tsz, Hong [GB/GB]; School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT (GB). (74) Agent: TURNER, James, Arthur, D. Young & Co., 21 New Fetter Lane, London EC4A 1DA (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published Without international search report and to be republished upon receipt of that report.	

(54) Title: MATERIAL DEPOSITION

(57) Abstract

A method of depositing a material on a substrate comprises the steps of: (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate; (b) applying an electric field between the outlet and the substrate; and (c) generating a flame between the outlet and the substrate so that the stream of droplets of the precursor liquid from the outlet pass through the flame before reaching the substrate.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

MATERIAL DEPOSITION

This invention relates to material deposition, for example as a film or layer on a substrate, or as a powder.

5 The applications of materials such as ceramics as structural coatings and functional electronic films are expanding rapidly. Various deposition techniques such as chemical vapour deposition (CVD), physical vapour deposition (PVD), flame spraying deposition (FSD), combustion chemical vapour deposition (CCVD) and sol-gel deposition have been developed or investigated.

10 Both CVD and PVD involve the use of sophisticated and expensive deposition chambers and/or vacuum systems. Applications of CVD and PVD methods to ceramic films are limited to coating processes in which the available film thickness and coating areas are relatively small.

15 It is often difficult to control the stoichiometry of multicomponent oxide films with CVD, and problems can also arise due to differences in vapour pressure of the CVD reagents and the low growth rate of the CVD films.

PVD methods such as radio frequency (RF) sputtering tend to give low deposition rates and poor yields. Reactive magnetic sputtering and ion beam sputtering need expensive equipment and skilled operators.

20 Flame synthesis deposition produces films with morphology, microstructure and electrical properties dependent on the temperature of the substrate, the coating concentration, the carrier gas flow rate and so on. Control of all of these variables to achieve a desired coating is difficult.

25 This invention addresses these problems by providing a deposition technique which at least alleviates some of the disadvantages of the prior art.

This invention provides a method (and a corresponding apparatus) for depositing a material on a substrate, the method comprising the steps of:

- (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate;
- 30 (b) applying an electric field between the outlet and the substrate; and
- (c) generating a flame between the outlet and the substrate so that at least a portion of the stream of droplets of the precursor liquid from the

outlet pass through the flame before reaching the substrate.

The invention provides a new technique which, in at least preferred embodiments, involves spraying atomised precursor droplets into a flame while providing an electric field between the precursor outlet and the substrate, so that the precursor forms a charged aerosol which undergoes combustion and/or chemical reactions in the vapour phase in the vicinity of the substrate. This can result in the formation of a stable solid film with good adhesion onto the substrate.

The invention will now be described, by way of example only, with reference to the accompanying drawings, throughout which like parts are described by like references and in which Figure 1 is a schematic diagram of a deposition apparatus.

Figure 1 schematically illustrates a deposition apparatus comprising a coaxial nozzle assembly 10 having a liquid precursor delivery capillary 20, a first coaxial passage 30 for cold air, nitrogen or other gases, and a second coaxial passage 40 for liquid or gaseous fuel.

The precursor can be, for example, one of the precursors listed in WO97/21848, with or without the catalyst described in that document. Many other precursors can be used as appropriate for the desired deposition, such as precursors known from the field of flame synthesis deposition (see publication reference 1).

The fuel may be a mixture of oxygen and acetylene, or another appropriate fuel such as fuels known from the field of flame synthesis deposition.

A high voltage source 45 maintains an electric field between the nozzle assembly 10 and a substrate 50. The potential difference between these two parts may be, for example, within the approximate ranges described in WO97/21848, such as in the approximate range of 5 - 30 kV.

The precursor liquid is sprayed towards a region 55 of the substrate 50 from an outlet 60 of the capillary 20. The fuel is ignited so that an annular combustion region 70 is generated. The extent of this combustion region can be controlled by controlling the fuel flow rate, the distance between the nozzle assembly 10 and the substrate 50, the amount and flow rate of cold gases in the passage 30, and the applied electric field.

Decomposition and/or chemical reaction of the precursor (e.g. a sol to gel transition) occurs in a higher temperature region of overlap between the spray of

precursor from the outlet 60 and the combustion region 70. Deposition occurs in or beneath this overlap zone. So, by controlling the extent of the combustion region as described above, the deposition on the substrate can be controlled, and premature reaction or decomposition can be avoided (a problem in many prior art flame deposition techniques, leading to non-uniform deposition).

Either polarity of electric field can be used, or a periodically or occasionally alternating field can be employed. A thermocouple can be used to monitor the temperature of the substrate.

An optional mesh 90 helps to remove soot from the flame and so help to provide a high temperature (blue) flame.

A further optional annular electrode connectable to the high voltage supply 45 at an intermediate potential between that of the nozzle and that of the substrate can be used to steer the deposition onto a required area.

The technique is also applicable to premixed fuel and precursor systems. However, non premixed systems are preferred as this gives greater control of the deposition temperature and helps to avoid premature decomposition.

The technique can be used to manufacture metal oxide and non-oxide materials; to fabricate pure, doped, multicomponent or multiphase materials; to manufacture materials with dense, porous or a combination of dense and porous structures; to manufacture composite, multilayer and compositionally graded structures; to produce thin or thick films; for rapid prototyping of net shape and near net shape components; or to coat planar or tubular substrates or other complex shaped components. The process can be scaled up for large area or mass production. This can be achieved using multiple flame / electrostatic units. For accurate deposition and process control, the process can be automated.

Conductive or non-conductive substrates can be used. For non-conductive substrates, the conductivity can be improved by having a conductive backing holder.

The process can be performed in an open atmosphere or in an inert / controlled atmosphere. For example, oxide-based structures can be deposited in an open atmosphere, or non oxides such as sulphides, carbides etc can be produced in a controlled atmosphere. Deposition can take place at atmospheric or a different pressure.

The chemistry of the precursor(s) can be adjusted so that once the chemical reaction starts to take place, a self-assisted reaction occurs. This can reduce the requirements for fuel while still achieving the required deposition temperature for a particular material.

5 The electric field helps to reduce the loss of precursor to the surroundings by directing the precursor to the deposition surface, a clear advantage over conventional flame-based techniques.

10 The deposition can be controlled by one or more of the following: the flow rate of the cold gas; the electric field strength; the fuel and its flow rate; the separation of the nozzle assembly from the substrate; the chemistry, concentration and flow rate of the precursor; and the deposition pressure.

15 Embodiments of the invention allow the use of simple, flexible and/or mobile equipment. The process can be relatively safe by the use of sol precursors and/or water based precursors. The process can give rise to an advantageously low flame / deposition temperature for crystalline materials (e.g. 550-800°C for $\text{Y}_2\text{O}_3\text{-ZrO}_2$). Dense films tend to require a sol precursor, whereas porous films may be based on sol or water based precursors. The consumption of precursor can be relatively low, e.g. 1 ml of 0.05M solution to generate a 1 micron film measuring 1cm x 1cm. The process can be a single step without the need for a subsequent heat treatment.

20 Powders can be formed by allowing the precursor's chemical reaction to solid to take place above the substrate. The substrate is then deposited with discrete powder particles which can be collected later from the substrate surface. Powder generation can be improved by employing gas condensation techniques and a cooled collecting substrate.

25 In a further embodiment, the substrate can be mounted on a moveable table or XY positioner (not shown) under the control of, for example a computer aided design (CAD) system (not shown) to allow a three dimensional object to be constructed layer by layer. This can be used in, for example, rapid prototyping systems.

PUBLICATION REFERENCES

1. Choy, K L, "Flame Assisted Vapour Deposition of Ceramic Films and Coatings", British Ceramic Proceedings, The Institute of Materials (1995), pp65-74
2. Hunt, A T et al, Applied Physics 63 (1993) No 2, pp266-268

The following patent documents are also mentioned as background art:
WO97/21848, GB-A-2 192 901, GB-A-2 162 861, EP-A-0 103 505, US-A-5 652 021,
US-A-5 534 311 and SE-A-9504410.

CLAIMS

1. A method of depositing a material on a substrate, the method comprising the steps of:
 - 5 (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate;
 - (b) applying an electric field between the outlet and the substrate; and
 - (c) generating a flame between the outlet and the substrate so that at least a portion of the stream of droplets of the precursor liquid from the
10 outlet pass through the flame before reaching the substrate.
2. A method according to claim 1 wherein the material is a ceramic material.
3. A method according to claim 1 or claim 2 wherein the material is a
15 multicomponent oxide material.
4. A method according to any one of the preceding claims, comprising the step of:
 - (d) heating the substrate.
20
5. A method according to any one of the preceding claims, in which the precursor liquid is a sol precursor solution.
6. A method according to any one of the preceding claims, comprising the step
25 of moving the substrate and/or the outlet during deposition so that a three-dimensional structure is deposited as a series of overlying deposited layers.
7. A method according to any one of the preceding claims, comprising
30 controlling a region of deposition by varying one or more of the rate of flow of fuel to provide the flame, the separation between the outlet and the substrate and the electric field between the outlet and the substrate.

8. A method according to any one of the preceding claims, comprising the step of providing a flow of cold gas in a direction from the outlet towards the substrate.

9. Apparatus for depositing a material on a substrate, the apparatus comprising:

- 5
- (a) an outlet;
 - (b) a precursor supply operable to pass a precursor liquid through the outlet to generate a stream of droplets of the precursor liquid directed towards the substrate;
 - 10 (c) an electrical supply for applying an electric field between the outlet and the substrate; and
 - (d) a burner for generating a flame between the outlet and the substrate so that at least a portion of the stream of droplets of the precursor liquid from the outlet pass through the flame before reaching the substrate.

15 10. Apparatus according to claim 9, comprising a coaxial outlet assembly having a plurality of coaxial outlets, one of the coaxial outlets carrying the precursor liquid and another of the coaxial outlets carrying fuel to provide the flame.

20 11. Apparatus according to claim 10, in which another coaxial outlet is arranged to carry a flow of cold gas.

12. Apparatus according to claim 10 or claim 11, in which the precursor liquid is carried by a central outlet of the coaxial outlet assembly.

25 13. Apparatus according to any one of claims 9 to 12, comprising a mesh disposed between the precursor liquid outlet and the substrate.

30 14. Apparatus according to any one of claims 9 to 13, comprising an electrode at an electric potential between the potential of the precursor outlet and the potential of the substrate and disposed between the precursor outlet and the substrate.

15. Apparatus according to claim 14, in which the electrode is an annular

electrode.

16. Apparatus according to any one of claims 9 to 15, comprising a positioner for altering the relative position of the precursor outlet and the substrate.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



COPY
REPLACED BY
PART 34 AMDT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23C	A2	(11) International Publication Number: WO 99/29917
		(43) International Publication Date: 17 June 1999 (17.06.99)

(21) International Application Number: PCT/GB98/03636
(22) International Filing Date: 7 December 1998 (07.12.98)

(30) Priority Data:
9725878.4 5 December 1997 (05.12.97) GB

(71) Applicant (for all designated States except US): IMPE-
RIAL COLLEGE OF SCIENCE, TECHNOLOGY AND
MEDICINE [GB/GB]; Sheffield Building, Exhibition Road,
London SW7 2AZ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CHOY, Kwang-Leong
[MY/GB]; 35 Blondvil Street, Cheylesmeore, Coventry CB3
5EQ (GB). CHANG, Isaac, Tsz, Hong [GB/GB]; School
of Metallurgy and Materials, University of Birmingham,
Edgbaston, Birmingham B15 2TT (GB).

(74) Agent: TURNER, James, Arthur, D. Young & Co., 21 New
Fetter Lane, London EC4A 1DA (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP,
KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK,
MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU,
ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG,
ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI,
FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE,
SN, TD, TG).

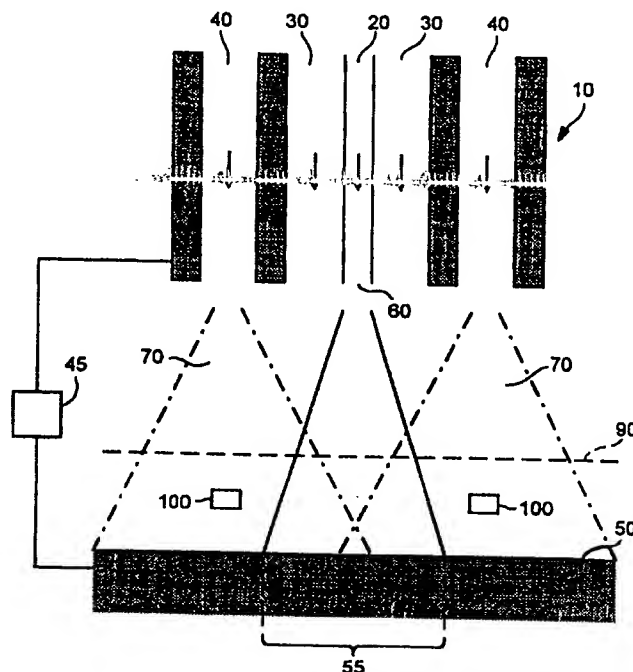
Published

Without international search report and to be republished
upon receipt of that report.

(54) Title: MATERIAL DEPOSITION

(57) Abstract

A method of depositing a material on a substrate comprises the steps of: (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate; (b) applying an electric field between the outlet and the substrate; and (c) generating a flame between the outlet and the precursor liquid from the outlet pass through the flame before reaching the substrate.





.

.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China			PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		



1
2

422 Rec'd PCT/PTO 01 JUN 2000

1/PART

MATERIAL DEPOSITION

This invention relates to material deposition, for example, as a film or layer on a substrate or as a powder.

5 The application of materials such as ceramics as structural coatings and functional electronic films is expanding rapidly. Various desposition techniques such as chemical vapour deposition (CVD), physical vapour deposition (PVD), flame synthesis deposition (FSD), combustion chemical vapour deposition (CCVT) and sol-gel deposition have been developed or investigated.

10 Both CVD and PVD techniques involve the use of sophisticated and expensive deposition chambers and/or vacuum systems. The application of CVD and PVD techniques to deposit ceramic films is limited to coating processes in which the film thicknesses and coating areas are relatively small.

15 It is often difficult to control the stoichiometry of multicomponent oxide films deposited by CVD techniques, and problems can also arise due to differences in the vapour pressures of the CVD reagents and the low growth rate of CVD films.

PVD techniques such as radio frequency (RF) sputtering tend to give low deposition rates and poor yields, and reactive magnetic sputtering and ion beam sputtering need expensive equipment and skilled operators.

20 FSD techniques produce films with a morphology, microstructure and electrical properties which are dependent on the temperature of the substrate, the coating concentration, the carrier gas flow rate and so on. Control of all of these variables to achieve a desired coating is difficult.

25 Reference is also made to Hunt *et al*, Applied Physics 63 (1993), No 2, pages 266 to 268, WO-A-97/21848, GB-A-2192901, GB-A-2162861, EP-A-0103505, US-A-5652021, US-A-5534311 and SE-A-9504410.

This invention addresses these problems by providing a deposition technique which at least alleviates some of the disadvantages of the prior art.

30 This invention provides a method of depositing material on a substrate, comprising the steps of: delivering from an outlet a stream of droplets of a precursor liquid towards a substrate; applying an electric field between the outlet and the substrate; and generating a flame between the outlet and the substrate such that at least

a portion of the stream of droplets of the precursor liquid passes through the flame before reaching the substrate and the precursor liquid is chemically reacted and/or decomposed to provide the deposited material.

This invention also provides an apparatus for depositing material on a substrate, comprising: a substrate holder for holding a substrate; a nozzle assembly including an outlet from which a stream of droplets of a precursor liquid is in use delivered to a substrate; a precursor supply for supplying a precursor liquid to the nozzle assembly; an electrical supply for applying an electric field between the outlet and the substrate; and a burner for generating a flame between the outlet and the substrate and being configured such that in use at least a portion of the stream of droplets of the precursor liquid passes through the flame before reaching the substrate and the precursor liquid is chemically reacted and/or decomposed to provide the deposited material.

In a preferred embodiment the material is a ceramic material.

This invention provides a new technique which, in at least preferred embodiments, involves spraying atomised precursor droplets into a flame while providing an electric field between the precursor outlet and the substrate, so that the precursor forms a charged aerosol which undergoes combustion and/or chemical reaction in the vapour phase in the vicinity of the substrate and allows for the formation of a stable solid film with good adhesion to the substrate.

This invention will now be described, ~~by way of example only, with reference~~ to the accompanying drawings, throughout which like parts are described by like references, and in which Figure 1 is a schematic diagram of a deposition apparatus.

Figure 1 schematically illustrates a deposition apparatus comprising a coaxial nozzle assembly 10 having a liquid precursor delivery capillary 20, a first coaxial passage 30 for cold air, nitrogen or other gases, and a second coaxial passage 40 for liquid or gaseous fuel.

The precursor can be, for example, one of the precursors listed in WO-A-97/21848, with or without the mentioned catalyst. Many other precursors can be used as appropriate for the desired deposition, such as precursors known from FSD techniques as disclosed by Choy in "Flame Assisted Vapour Deposition of Ceramic



Films and Coatings", British Ceramic Proceedings, The Institute of Materials (1995), pages 65 to 74.

The fuel may be a mixture of oxygen and acetylene, or another appropriate fuel, such as fuels known from FSD techniques.

5 A high voltage source 45 maintains an electric field between the nozzle assembly 10 and a substrate 50. The potential difference may be, for example, within the approximate ranges described in WO-A-97/21848, typically in the approximate range of from 5 to 30 kV.

10 The precursor liquid is sprayed towards a region 55 of the substrate 50 from an outlet 60 of the capillary 20. The fuel is ignited so that an annular combustion region 70 is generated. The extent of this combustion region can be controlled by controlling the fuel flow rate, the distance between the nozzle assembly 10 and the substrate 50, the amount and flow rate of cold gases in the passage 30, and the applied electric field.

15 Decomposition and/or chemical reaction of the precursor, for example, a sol-gel transition, occurs in a higher temperature overlap zone between the spray of precursor from the outlet 60 of the capillary 20 and the combustion region 70. Deposition occurs in or beneath this overlap zone. So, by controlling the extent of the combustion region as described above, the deposition on the substrate 50 can be controlled, and premature reaction or decomposition, which is a problem in many prior art FSD techniques leading to non-uniform deposition, can be avoided.

20 Either ~~polarity of electric field can be used~~, or a periodically or occasionally alternating field can be employed. A thermocouple can be used to monitor the temperature of the substrate 50.

25 The apparatus preferably includes a mesh 90 which assists in removing soot from the flame and so provide a high temperature (blue) flame.

The apparatus preferably includes a further annular electrode 100 connected to the high voltage supply 45 at an intermediate potential between that of the nozzle assembly 10 and the substrate 50 to steer the material being deposited onto a required area of the substrate 50.

30 The technique is also applicable to premixed fuel and precursor systems. However, non-premixed systems are preferred as these systems give greater control of the deposition temperature and assist in avoiding premature decomposition.



The technique can be used to manufacture metal oxide and non-oxide materials; to manufacture pure, doped, multicomponent or multiphase materials; to manufacture materials with dense, porous, or a combination of dense and porous structures; to manufacture composite, multilayer and compositionally-graded structures; to produce thin or thick films; for rapid prototyping of net shape and near net shape components; or to coat planar or tubular substrates or other complex shaped components.

The technique can be scaled up for large area or mass production by using multiple flame/electrostatic units. For accurate deposition and process control, the process can be automated.

The substrate 50 can be conductive or non-conductive. For non-conductive substrates, the conductivity can be improved by utilizing a conductive backing holder.

The technique can be performed in an open atmosphere or in an inert/controlled atmosphere. For example, oxide-based structures can be deposited in an open atmosphere, and non-oxide structures, such as sulphides, carbides, etc, can be deposited in a controlled atmosphere. Deposition can take place at atmospheric or a different pressure.

The chemistry of the precursors can be adjusted so that once the chemical reaction starts to take place, a self-assisted reaction occurs. This can reduce the requirements for fuel, while still achieving the required deposition temperature for a particular material.

The electric field reduces the loss of precursor to the surroundings by directing the precursor to the deposition surface. This is a clear advantage over conventional flame-based techniques.

The deposition can be controlled by one or more of the following: the flow rate of the cold gas; the electric field strength; the fuel and its flow rate; the separation of the nozzle assembly from the substrate; the chemistry, concentration and flow rate of the precursor; and the deposition pressure.

Embodiments of the invention allow the use of simple, flexible and/or mobile equipment. The technique can be made relatively safe by the use of sol precursors and/or water based precursors. The process can give rise to an advantageously low flame/deposition temperature for crystalline materials, for example from 550 to 800 °C



for $Y_2O_3-ZrO_2$. Dense films tend to require a sol precursor, whereas porous films may be based on sol or water based precursors. The consumption of precursor can be relatively low, for example, 1 ml of 0.05 M solution to generate a 1 μm film measuring 1 cm x 1 cm. Furthermore, the deposition can be performed in a single step without
5 the need for a subsequent heat treatment.

Powders can be formed by providing for the chemical reaction of the precursor to the solid phase to take place above the substrate 50. With this configuration, the substrate 50 is deposited with discrete powder particles which can be later collected. Powder generation can be improved by employing gas condensation techniques and a
10 cooled collecting substrate.

In a further embodiment, the substrate 50 can be mounted on a movable table or XY positioner under the control of, for example, a computer aided design (CAD) system to allow three-dimensional objects to be constructed layer by layer. This can be used in, for example, rapid prototyping systems.



CLAIMS

1. A method of depositing material on a substrate, comprising the steps of:
delivering from an outlet a stream of droplets of a precursor liquid towards a
substrate;
5 applying an electric field between the outlet and the substrate; and
generating a flame between the outlet and the substrate such that at least a
portion of the stream of droplets of the precursor liquid passes through the
flame before reaching the substrate and the precursor liquid is chemically
reacted and/or decomposed to provide the deposited material.
10
2. The method according to claim 1, wherein the flame generation step comprises
the step of delivering from a second outlet an annular flow of fuel about the
stream of droplets such as to provide an annular flame combustion region
through which at least the portion of the stream of droplets passes before
15 reaching the substrate.
3. The method according to claim 2, wherein the annular flow of fuel is a
diverging flow.
- 20 4. The method according to claim 2 or 3, wherein the first and second outlets are
coaxial.
5. The method according to any of claims 1 to 4, wherein the stream of droplets is
provided as a diverging spray.
25
6. The method according to any of claims 1 to 5, further comprising the step of
delivering a flow of cold gas in the direction from the first outlet towards the
substrate.

7. The method according to claim 6 when appendant upon claim 2, wherein the flow of cold gas is delivered from a third outlet as an annular flow about the stream of droplets and within the annular flow of fuel.
- 5 8. The method according to claim 7, wherein the first and third outlets are coaxial.
9. The method according to any of claims 1 to 8, wherein the material is a ceramic material.
- 10 10. The method according to any of claims 1 to 9, wherein the material is a multicomponent oxide material.
11. The method according to any of claims 1 to 10, further comprising the step of heating the substrate.
- 15 12. The method according to any of claims 1 to 11, wherein the precursor liquid is a sol precursor solution.
13. The method according to any of claims 1 to 12, further comprising the step of moving one or both of the substrate and the first outlet during deposition so as
20 ~~to deposit a three-dimensional~~ structure as a series of overlying layers.
14. The method according to any of claims 1 to 13, further comprising the step of controlling the region of deposition by varying one or more of the rate of flow
25 of the fuel, the separation between the first outlet and the substrate and the electric field between the first outlet and the substrate.
15. The method according to any of claims 1 to 14, wherein the material is deposited as a powder and the chemical reaction and/or decomposition occurs
30 away from the substrate.



16. The method according to any of claims 1 to 14, wherein the material is deposited as a solid film and the chemical reaction and/or decomposition occurs in the vicinity of the substrate.
- 5 17. An apparatus for depositing material on a substrate, comprising:
a substrate holder for holding a substrate;
a nozzle assembly including an outlet from which a stream of droplets of a precursor liquid is in use delivered to a substrate;
a precursor supply for supplying a precursor liquid to the nozzle assembly;
10 an electrical supply for applying an electric field between the outlet and the substrate; and
a burner for generating a flame between the outlet and the substrate and being configured such that in use at least a portion of the stream of droplets of the precursor liquid passes through the flame before reaching the substrate and the
15 precursor liquid is chemically reacted and/or decomposed to provide the deposited material.
18. The apparatus according to claim 17, wherein the burner is provided by the
20 nozzle assembly and the nozzle assembly includes a second outlet from which ~~an annular flow of fuel is in use~~ delivered such as to provide an annular flame combustion region through which at least the portion of the stream of droplets passes before reaching the substrate, and further comprising a fuel supply for supplying fuel to the nozzle assembly.
- 25 19. The apparatus according to claim 18, wherein the first and second outlets are coaxial.
20. The apparatus according to claim 18 or 19, wherein the nozzle assembly further
30 comprises a third outlet disposed between the first and second outlets from which an annular flow of cold gas is in use delivered.



21. The apparatus according to claim 20, wherein the first and third outlets are coaxial.
22. The apparatus according to any of claims 18 to 21, wherein the first outlet is a central outlet.
23. The apparatus according to any of claims 17 to 22, further comprising a mesh disposed between the first outlet and the substrate.
24. The apparatus according to any of claims 17 to 23, further comprising an electrode at an electric potential between the potential of the first outlet and the substrate and disposed between the first outlet and the substrate.
25. The apparatus according to claim 24, wherein the electrode is an annular electrode.
26. The apparatus according to any of claims 17 to 25, further comprising a positioner for altering the relative position of the first outlet and the substrate.
27. The apparatus according to any of claims 17 to 26, where configured such that the chemical reaction and/or decomposition occurs away from the substrate so as to provide the material as a powder.
28. The method according to any of claims 17 to 26, where configured such that the chemical reaction and/or decomposition occurs in the vicinity of the substrate so as to provide the material as a solid film.



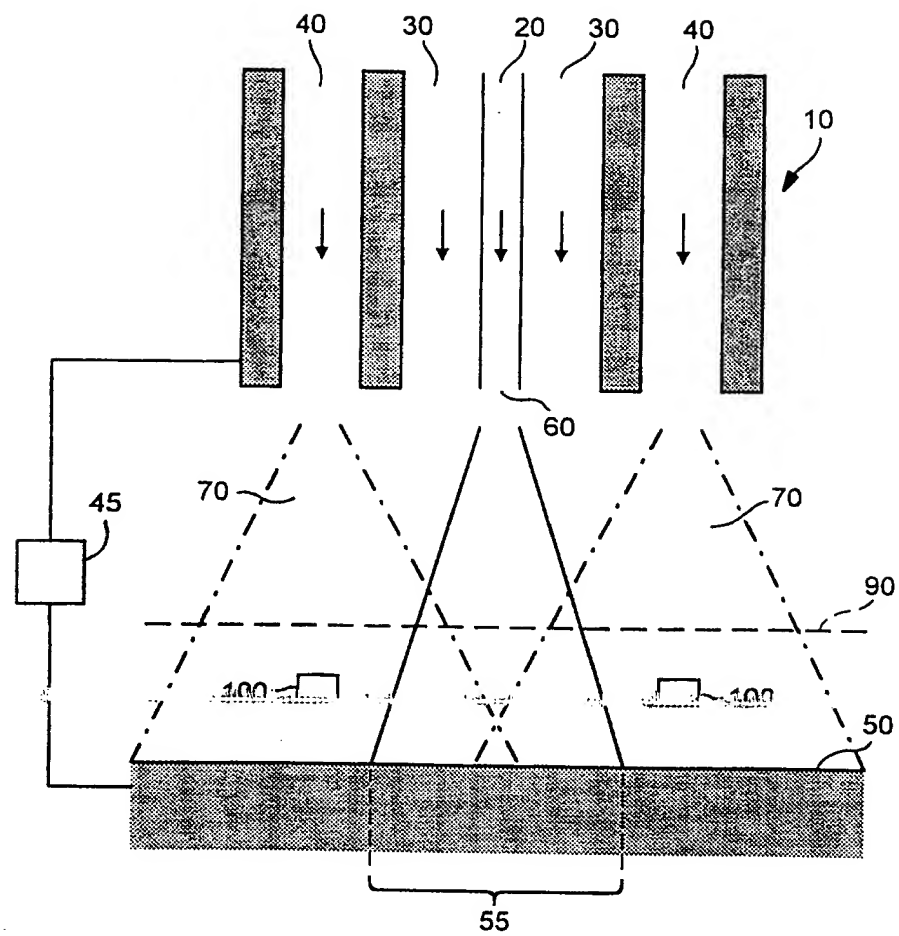
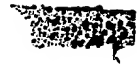


FIG. 1

422 Rec'd PCT/PTO 01 JUN 2000



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 6 : C23C 16/44</p>	<p>A3</p>	<p>(11) International Publication Number: WO 99/29917</p> <p>(43) International Publication Date: 17 June 1999 (17.06.99)</p>
<p>(21) International Application Number: PCT/GB98/03636</p> <p>(22) International Filing Date: 7 December 1998 (07.12.98)</p> <p>(30) Priority Data: 9725878.4 5 December 1997 (05.12.97) GB</p> <p>(71) Applicant (for all designated States except US): IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY AND MEDICINE [GB/GB]; Sherfield Building, Exhibition Road, London SW7 2AZ (GB).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): CHOY, Kwang-Leong [MY/GB]; 35 Blondvil Street, Cheylesmore, Coventry CB3 5EQ (GB). CHANG, Isaac, Tsz, Hong [GB/GB]; School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT (GB).</p> <p>(74) Agent: TURNER, James, Arthur; D. Young & Co., 21 New Fetter Lane, London EC4A 1DA (GB).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p> <p>(88) Date of publication of the international search report: 22 July 1999 (22.07.99)</p>
<p>(54) Title: MATERIAL DEPOSITION</p>		
<p>(57) Abstract</p> <p>A method of depositing a material on a substrate comprises the steps of: (a) passing a precursor liquid through an outlet to generate a stream of droplets of the precursor liquid directed towards the substrate; (b) applying an electric field between the outlet and the substrate (50) so that the stream of droplets of the precursor liquid from the outlet (60) pass through the flame before reaching the substrate (50).</p>		



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	ES	Spain	LS	Lesotho	SI	Slovenia
AT	Austria	FI	Finland	LT	Lithuania	SK	Slovakia
AU	Australia	FR	France	LU	Luxembourg	SN	Senegal
AZ	Azerbaijan	GA	Gabon	LV	Latvia	SZ	Swaziland
BA	Bosnia and Herzegovina	GB	United Kingdom	MC	Monaco	TD	Chad
BB	Barbados	GE	Georgia	MD	Republic of Moldova	TG	Togo
BE	Belgium	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BF	Burkina Faso	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BG	Bulgaria	GR	Greece			TR	Turkey
BJ	Benin	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BR	Brazil	IE	Ireland	MN	Mongolia	UA	Ukraine
BY	Belarus	IL	Israel	MR	Mauritania	UG	Uganda
CA	Canada	IS	Iceland	MW	Malawi	US	United States of America
CF	Central African Republic	IT	Italy	MX	Mexico	UZ	Uzbekistan
CG	Congo	JP	Japan	NE	Niger	VN	Viet Nam
CH	Switzerland	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CI	Côte d'Ivoire	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CM	Cameroon	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CN	China			PL	Poland		
CU	Cuba	KR	Republic of Korea	PT	Portugal		
CZ	Czech Republic	KZ	Kazakhstan	RO	Romania		
DE	Germany	LC	Saint Lucia	RU	Russian Federation		
DK	Denmark	LI	Liechtenstein	SD	Sudan		
EE	Estonia	LK	Sri Lanka	SE	Sweden		
		LR	Liberia	SG	Singapore		



INTERNATIONAL SEARCH REPORT

In International Application No
PCT/GB 98/03636

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C16/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 005, no. 054 (C-050), 15 April 1981 & JP 56 005337 A (HITACHI LTD; OTHERS: 01), 20 January 1981 see abstract	1,2,6,7, 9-12,16
Y		
A		3,4,14, 15 8
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 143 (C-117), 3 August 1982 & JP 57 067038 A (NIPPON TELEGR & TELEPH CORP), 23 April 1982 see abstract	1,2,6,9, 16

	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

26 May 1999

Date of mailing of the international search report

02/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ekhuit, H



INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/GB 98/03636

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 098, no. 001, 30 January 1998 & JP 09 235131 A (SHOWA ELECTRIC WIRE & CABLE CO LTD; NIPPON TELEGR & AMP; TELEPH CORP), 9 September 1997 see abstract ---	3,4
Y	PATENT ABSTRACTS OF JAPAN vol. 014, no. 227 (C-0718), 15 May 1990 & JP 02 055241 A (HITACHI CABLE LTD), 23 February 1990 see abstract ---	14,15
A	WO 97 21848 A (BAI WEI ;CHOY KWANG LEONG (GB); IMPERIAL COLLEGE (GB)) 19 June 1997 cited in the application ---	5
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 262 (C-608), 16 June 1989 & JP 01 065040 A (SUMITOMO ELECTRIC IND LTD), 10 March 1989 see abstract -----	13



INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/03636

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9721848 A	19-06-1997	GB 2308132 A	18-06-1997
		AU 1182997 A	03-07-1997
		CA 2240625 A	19-06-1997
		EP 0870075 A	14-10-1998

